Synthetic Methods

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Cooperation between Transition Metals and Lewis Acids: A Way To Activate H_2 and H−E bonds**

*Marc Devillard, Ghenwa Bouhadir, and Didier Bourissou**

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Following the pioneering contributions of Noyori and Shvo, metal–ligand cooperation has attracted considerable interest for activation and formation of chemical bonds under mild reaction conditions.[1] This approach is based on the active participation of an electron-rich ligand which typically features a heteroatom lone pair or a delocalized π system (Figure 1). It represents a valuable alternative to the typical oxidative addition/reductive elimination pathways. Such metal–ligand cooperation has been successfully employed in a wide range of catalytic processes and has allowed new transformations.

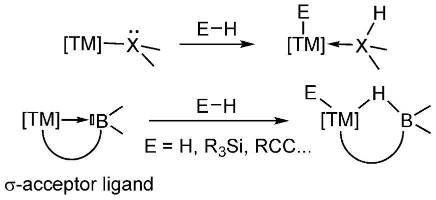
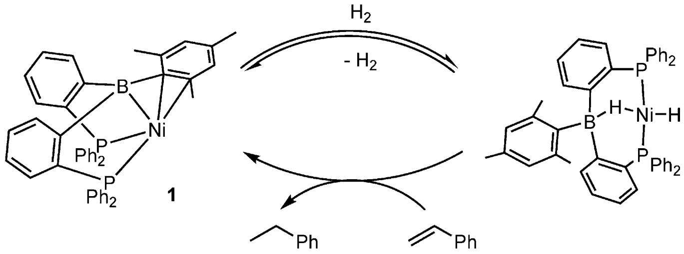


Figure 1. Activation of E−H bonds involving metal–ligand cooperativity.

The ability of Lewis acids (LAs) to bind to transition metals as σ-acceptor ligands was recognized early on and the respective ligands are usually referred as Z-type ligands. For a long time, complexes involving M→LA interactions remained extremely scarce, but chelating assistance has enabled significant progress over the last decade.[2] Accordingly, borane complexes, long considered as putative species, were unambiguously authenticated. The advent of ambiphilic ligands, in particular phosphine boranes, has clearly played a major role here, thus providing straightforward access to M→B interactions. The presence of a Lewis acid in the first coordination sphere of a transition metal offers very interesting possibilities in terms of reactivity. Thanks to fine-tuning of the ligand framework, complexes featuring relatively weak M→B interactions were shown recently to readily activate H−H, H−Si (silanes), and H−C (terminal alkynes) bonds. These reactions involve a new type of metal–ligand cooperation and opens new perspectives in catalysis.

A major breakthrough in the cooperation between transition metals and Lewis acids[3] was reported by Peters in 2012 (Scheme 1).[4] The diphosphine borane nickel complex



Scheme 1. Activation of H_2 by a diphosphine borane nickel complex and application to catalytic hydrogenation.

1 adopts a pyramidal geometry with η^3-BCC coordination[5] of the central BMes moiety. It displays an ideal balance between stability and reactivity. Indeed, H_2 is rapidly and reversibly activated under 1 atm at 25 °C. According to NMR spectroscopy and DFT calculations, the ensuing dihydrido nickel complex adopts *trans*-square-planar geometry and it is stabilized by a Ni-H-B bridging interaction. Then, H_2 can be efficiently transferred to styrene and this hydrogenation reaction can be achieved catalytically under mild reaction conditions. Importantly, when the Mes group at B is replaced by a Ph ring, the nickel complex features strong η^2-BC coordination and does not react with H_2 even under forcing conditions (days at 60 °C).

The role of the Lewis acid moiety was substantiated by mechanistic studies.[6] Replacing the Ph substituents at P by *i*Pr groups enabled characterization, by NMR spectroscopy, of the initially formed σ-H_2 complex before oxidative addition to nickel occurs. According to DFT calculations, cooperation between Ni and B is crucial: it significantly lowers the activation barrier, it stabilizes the ensuing dihydrido complex, and it facilitates the subsequent insertion of styrene. This

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[*] M. Devillard, Dr. G. Bouhadir, Dr. D. Bourissou
Université de Toulouse, UPS, LHFA
118 route de Narbonne, 31062 Toulouse (France)
and
CNRS, LHFA, UMR 5069
31062 Toulouse (France)
E-mail: dbouriss@chimie.ups-tlse.fr
Homepage: http://http://lhfa.cnrs.fr/index.php/equipes/lbpb

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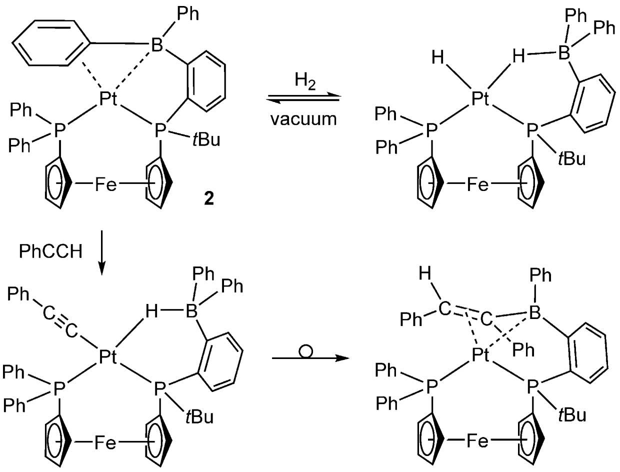
represents a new mode of metal–ligand cooperation which is conceptually reminiscent of the bifunctional activation encountered with frustrated Lewis pairs.[7] Formally, it is possible to consider that the electron-rich nickel center of **1** acts as a Lewis base while the borane moiety acts a Lewis acid.

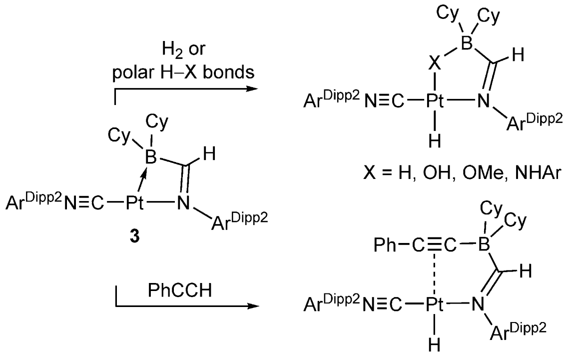
Such behavior was soon after extended to the activation of H_2 across a Fe→B interaction within a cage complex derived from a triphosphine borane ligand.[8a] Generalization to the activation of H–Si bonds of silanes ($PhSiH_3$, Ph_2SiH_2) was also substantiated and **1** was found to catalyze the hydrosilylation of a range of *para*-substituted benzaldehydes under mild reaction conditions (RT).[8b]

Very recently, Cowie and Emslie generalized and pushed forward such metal–Lewis acid cooperation (Scheme 2).[9] A multistep strategy was developed to install a pendant diphenylborane moiety on a diphosphine ferrocene framework. The derived platinum complex **2** displays η^3-BCC coordination (similar to the Ni complex **1**). Oxidative addition of H_2 occurs under mild reaction conditions (RT, 1 atm) and is reversible (under vacuum). According to spectroscopic data and DFT calculations, the resulting complex adopts a distorted square-planar geometry with one hydride bridging Pt and B. Catalytic hydrogenation could not be achieved in an effective and reproducible manner, but **2** was found to readily react with phenylacetylene. Oxidative addition of the C–H bond proceeds instantaneously at room temperature and is followed by an original rearrangement leading to η^3-BCC vinyl borane complexes. The structure of the new diphosphine borane ligand deserves some comment. The diphosphine ferrocene framework imparts strong coordination and prevents undesirable dissociation, while providing some flexibility. In addition, the rigid *o*-phenylene spacer positions the BPh_2 moiety ideally to interact with the first coordination sphere of platinum.



Scheme 2. Activation of E–H bonds by a borane-appended diphosphine ferrocene platinum complex.

Taking advantage of the bulky terphenyl isocyanide $Ar^{Dipp2}NC$ [Ar^{Dipp2} = 2,6-(2,6-(iPr)$_2C_6H_3)_2C_6H_3$], Figueroa and co-workers advanced the field further (Scheme 3).[10]



Scheme 3. Activation of E–H bonds by a (boryl)iminomethane platinum complex.

Dicyclohexylborane Cy_2BH readily adds to the isocyanide, either in its free form or once coordinated to platinum. As apparent from spectroscopic and crystallographic data, the ensuing complex **3** features a significant Pt→B interaction, despite the strain associated with the small NPtB bite angle (66°).[11] The presence of a single donor buttress in the ligand increases the flexibility towards incoming substrates and **3** was found to irreversibly activate H_2 (1 atm, RT). The C–H bond of phenylacetylene is also readily cleaved to give an original hydride complex in which the PhCC moiety is transferred to B and side-on coordinated to platinum. Last but not least, a variety of polar H–X bonds (X = O, N) have been activated by the Pt→B unit of **3**. The reactions are formal oxidative additions and lead to hydride complexes with hydroxide, methoxide, or anilide moieties bridging Pt and B.

In conclusion, ambiphilic ligands enable introduction of Lewis acids in the coordination sphere of transition metals in a controlled manner. This arrangement opens the route to a new type of metal–ligand cooperation involving Lewis acid assistance. Recent contributions by the groups of Peters, Emslie, and Figueroa have showcased the ability of boranes, while weakly coordinated as σ-acceptor ligands, to actively participate in the activation of H_2 and E–H bonds. These cutting-edge results will certainly stimulate research on cooperative activation of other strong σ-bonds. Here, the Lewis acid moiety may stabilize the resulting oxidative addition products, it may assist the activation process itself and it may also participate in subsequent transformations (by releasing a coordination site and thereby facilitating the reaction of incoming substrates).

Besides cooperative activation of σ bonds, complexes of ambiphilic ligands hold promise in other directions of catalytic relevance. In particular, the Lewis acid moiety can give direct access to zwitterionic complexes by abstraction of anionic co-ligands.[12]

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